

Synthesis and characterization of novel thiophene-based polybenzimidazole membrane for high-temperature fuel cells

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Abstract In this study, a new type of thiophene-based polybenzimidazole was synthesized by the condensation polymerization of 2,5-thiophene dicarboxylic acid and 3,3'-diaminobenzidine for high-temperature proton exchange membrane fuel cells. The resulting poly(benzimidazole-co-thiophene) (PBITH) membrane was prepared using the direct casting method at 200 °C in a hot press. The PBITH membranes were immersed in a 10 mol phosphoric acid (PA) solution for 2 weeks. The proton conductivity of the doped-PBITH (DPBITH) membrane increased with increasing temperature, and the maximum conductivity was 0.120 S cm^{-1} at 150 °C and 15 % relative humidity. The DPBITH showed higher proton conductivity than the doped-polybenzimidazole membrane due to the presence of additional thiophene heterocycles. Incorporation of the thiophene groups as an additional sulfur containing

heterocycle increased the basicity of the polymer backbone and enhanced the interaction between PA and the polymer.

Keywords Poly(benzimidazole-co-thiophene) · Membrane · Proton exchange membrane fuel cell · Proton conductivity · Mechanical properties · Thermal stability

1 Introduction

Proton exchange membrane fuel cells (PEMFCs) are highly beneficial for both automobile and stationary applications due to their broad range of energy generation ability. Nafion, the most widely accepted and commercialized membrane for PEMFC, possesses the disadvantage of low conductivity at high-temperature and low-humidity conditions. PEMFCs operating at low temperatures have several drawbacks, including CO catalyst poisoning, fuel crossover as well as water and heat management issues. These technical challenges can be overcome by operating the PEMFC at high temperatures. However, such conditions tend to decrease the thermochemical and mechanical stabilities of the polymeric materials [1].

Efforts have been made to develop several proton conducting membranes that can operate well above 100 °C. Among the membranes developed to date, acid–base types of membranes are considered to be potential candidates for high-temperature applications. Polymers bearing basic sites like ether, alcohol, imine, amide or imide groups act as proton acceptors and form ion pairs. Phosphoric and phosphonic acids are widely used to improve the proton conductivity of the membranes due to their amphoteric nature and their abilities to form dynamic hydrogen bond networks. In these networks, protons can be readily transferred by hydrogen bond-breaking and forming processes [2–4].

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Polybenzimidazole (PBI) membranes have currently been proposed as an alternative candidate for high-temperature PEMFCs because of their outstanding thermal, oxidative, chemical and hydrolytic stability at high temperatures. PBI does not conduct protons by itself. Hence, it is necessary to immerse the membranes in non-volatile acids in order to make it proton conducting. The non-volatile nature of phosphoric acid (PA) and high thermal stability of the polymer allow the acid-doped-PBI membrane to operate at temperatures up to 200 °C while maintaining acceptable proton conductivity. These advantages make PBI one of the most promising candidates for high-temperature PEMFCs [1, 5]. In recent years, extensive studies have been conducted to improve the technical properties of PBI membranes including the proton conductivity by modifying the surface, backbone and blending with other membranes [6–10]. Increasing the basicity of the polymer has been found to enhance the proton conductivity of the resulting membrane [11].

The aim of this study was to increase the basicity of the PBI-type membrane by replacing the benzene ring in the polymer unit with a thiophene ring. For this purpose, the poly(benzimidazole-co-thiophene) (PBITH) membrane was prepared by the condensation polymerization of 2,5-thiophene dicarboxylic acid (TDA) and 3,3'-diaminobenzidine (DAB). The resulting undoped and PA-doped membranes were characterized by spectroscopy, proton conductivity, morphology, thermal stability and mechanical properties of the membranes.

2 Experimental

2.1 Materials

DAB and PA were purchased from Tokyo Chemical Industry, Co. Ltd, Japan. TDA, methane sulfonic acid and phosphorus pentoxide were obtained from Sigma-Aldrich, USA. The Eaton's reagent (phosphorus pentoxide/methane sulfonic acid; PPMA, w/w: 1/10) was prepared as described in the literature [10, 12].

2.2 Synthesis of PBITH

The schematic depiction for the synthesis of PBITH is shown in Fig. S1 (supporting information). In a typical procedure, a three-necked 250-ml round-bottom flask was equipped with an overhead mechanical stirrer, a water-cooled condenser and a nitrogen-purge inlet and outlet. DAB (4.3 g, 0.02 mol) and TDA (3.4 g, 0.02 mol) were added to the flask followed by the addition of 60–70 ml PPMA. The reaction mixture was stirred using mechanical stirrer at 100 rpm and purged with dry nitrogen. The temperature of the reaction mixture

was controlled using a programmable temperature controller with ramp and soak features, and it was kept at 150 °C for 1 h. Then, the temperature was increased to 190 °C and maintained for 12 h to complete the polymerization. A small amount of the reaction mixture was poured into DI water and isolated as a brown mass. The brown mass was washed thoroughly with DI water and dried in a vacuum oven at 70 °C for 24 h to obtain the PBITH for further characterization and testing.

2.3 Membrane preparation and doping

The reaction mixture (from Sect. 2.2) was cooled to room temperature, and the membrane was prepared by the direct casting method. The reaction mixture was placed between two Teflon sheets and heated to 200 °C for 15 min at a pressure of 2 tons in a hot press (Model 3721, Carver Co., USA). The assembly was then cooled to room temperature under pressure. A fine thin membrane of PBITH was automatically separated out. This membrane was boiled with DI water for 24 h and then immersed in PA solution (10 mol) for 2 weeks for complete saturation of the PA-doping of the membrane [13]. During this process, the phosphorus pentoxide adsorbed on the membrane also gets hydrolyzed to PA in situ [14, 15]. The thickness of the membrane after doping was 100 µm. For a better comparison, the reference PBI membrane was also immersed in PA solution (10 mol) for 2 weeks to obtain complete saturation of the PA-doping of the membrane. The weight of membranes before and after doping was measured to calculate doping level.

2.4 Characterizations

Fourier transform infrared spectroscopy (FTIR) spectra were recorded on a Nicolet 6700 FTIR instrument (ThermoScientific, USA) at a frequency range of 500–4,000 cm^{-1} . The cryo-fractured samples were used for field emission scanning electron microscopy (FESEM) (S-4800, Hitachi, Japan) analysis. Thermogravimetric analysis (TGA) was carried out using Q50 TGA (TA Instruments, USA), at a heating rate of 10 °C min^{-1} in a nitrogen atmosphere. The mechanical properties of the membranes at room temperature were measured using a LR5 K universal testing machine (Lloyd Co, England) at a crosshead speed of 5 mm min^{-1} , according to the ASTM D-412.

The proton conductivities of the membranes were measured by the four-probe method using a BakkTech conductivity test cell in conjunction with a PGZ 301 Dynamic EIS Voltammeter (BakkTech LIC Co, USA). Temperature and humidification were controlled using a Globe Tech Computer Cell GT fuel cell test station. The relative humidity (RH) within the testing chamber was

controlled using a dew point system consisting of temperature regulation and a DI water inlet.

3 Results and discussion

3.1 FTIR analysis

The FTIR peaks at 3,338 and 3,261 cm^{-1} in the PBITH appeared due to the stretching vibrations of the non-hydrogen bonded and hydrogen bonded N–H groups, respectively (Fig. 1). However, the band broadening in the region of 2,400–3,000 cm^{-1} in the doped-DPBITH (DPBITH) may be due to the protonation of nitrogen in the imidazole rings. The bands at 1629, 1582, 1434 and 1400 cm^{-1} were assigned to the $\text{C}=\text{N}_{\text{str}}$ and $\text{C}=\text{C}_{\text{str}}$ vibrations of PBITH. The positions of these peaks slightly changed after doping, and their intensities were reduced due to the changes in their chemical environment after doping [9–13]. The peaks in the wave number ranges 1,411–1,580 cm^{-1} and at 800 cm^{-1} were attributed to the thiophene ring and stretching vibrations of the 2,5-substituted thiophene ring, respectively [16]. The extra peaks at 962 and 1,112 cm^{-1} were the characteristic peaks of hydrogen phosphate and PA groups, respectively [9–13].

3.2 Morphological analysis

The FESEM images of the cryo-fractured PBITH and DPBITH membranes are shown in Fig. 2. Clear differences in the structure of the pulled-out fibers and the surface roughness were observed between the undoped and doped membranes. The smooth fracture surface in the DPBITH compared to the PBITH indicated a reduction in the

intramolecular cohesive forces between PBITH polymer chains, after doping with H_3PO_4 . This difference was due to the strong intramolecular H-bonding between the imidazolium and thiophene rings of PBITH. These intramolecular H-bondings were reduced due to the presence of H_3PO_4 molecules.

3.3 Thermogravimetric analysis (TGA) and doping level

The synthesized PBITH showed high thermal stability as evident from its TGA and DTG curves (supporting information, Fig. S2). A substantial amount of weight loss was observed at temperatures above 400 °C. The initial weight loss below 150 °C in the TGA curves of DPBITH was due to the presence of absorbed water. The degradation of PA involved two steps commencing at 160 and 600 °C, respectively. After repeated washing in hot DI water, trace amounts of PA still remained in the DPBITH membranes (apparent from the corresponding weight losses in the TGA curve). The trend in weight loss for both PBITH and DPBITH was fairly similar. However, a larger amount of weight loss was evident in the case of DPBITH relative to the PBITH membranes, which was due to the presence of the PA in the DPBITH. The measured doping level of the DPBITH was 9.6 mol H_3PO_4 per polymer repeat unit (76 wt% H_3PO_4).

3.4 Mechanical properties

Table 1 lists the mechanical properties of the PBITH and DPBITH membranes. The tensile strength (TS), elongation at break (EB) and Young's modulus (YM) of the PBITH membrane were 9.3 MPa, 3.2 % and 295.0 MPa, respectively. Doping of the membrane resulted in a decrease in the TS and YM, but with an increase in EB. This was likely due to the plasticizing effect of PA, as observed for similar PBI-type membranes [13, 17]. This finding was in good agreement with our FESEM observation that doping of PBITH membrane resulted in a decrease in the intramolecular interaction due to the presence of PA.

3.5 Proton conductivity

Figure 3 shows the effect of RH on the proton conductivity of DPBITH membranes and the doped-PBI membrane (doping level: 6.0 mol H_3PO_4) obtained from Ref. [17]. The proton conductivity of the DPBITH membrane increased with temperature and RH. Interestingly, the proton conductivities of the DPBITH membranes measured at different temperatures (120–150 °C) were higher than those of the doped-PBI membrane measured at 150 °C. The highest conductivities of the doped-PBI and DPBITH membranes

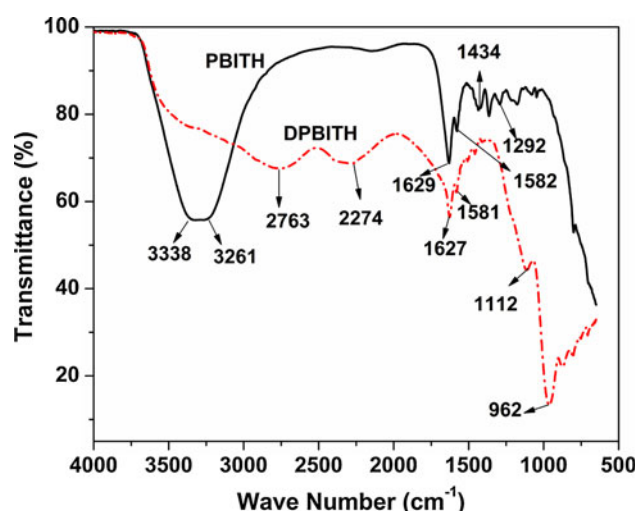


Fig. 1 FT-IR spectra of PBITH and DPBITH membranes

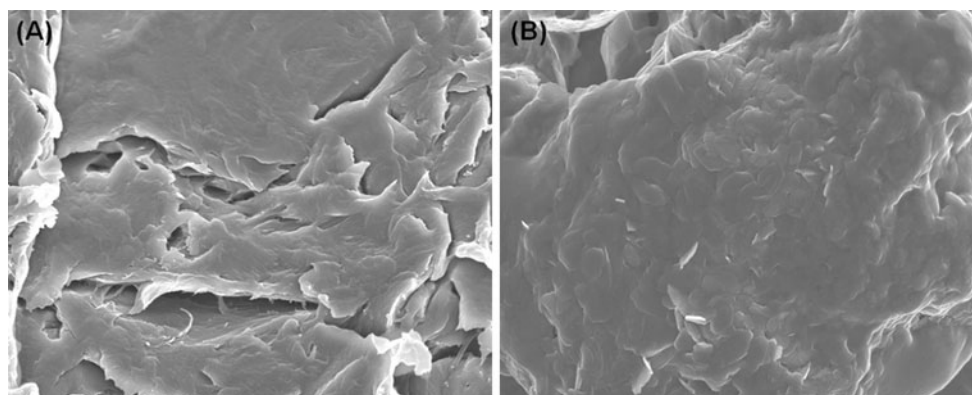
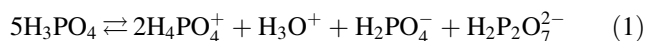


Fig. 2 FESEM images of the cryo-fractured surfaces of **a** PBITH and **b** DPBITH

Table 1 Mechanical properties of pure PBITH and DPBITH membranes

Sample	Stress at break (MPa)	Elongation at break (%)	Young's modulus (MPa)
PBITH	9.3	3.2	295.0
DPBITH	5.6	4.9	113.8

were 0.045 and 0.120 S cm⁻¹, respectively at 150 °C and 15 % RH. The proton conductivity of the DPBITH membrane was much higher than the reported values for PBI (0.060 S cm⁻¹) [18] and for sulfonated PBI membrane (0.003 S cm⁻¹) [19]. This suggests that the sulfur containing heterocycles in the polymer backbone enhances its basicity thereby increasing its interaction with PA. The high conductivity of DPBITH even at low RH was assigned to the self-ionization and self-dehydration mechanism of H₃PO₄ (Eq. 1). Moreover, increasing RH enhances the membrane conductivity due to the dissociation of PA and increased number of charge carriers (Eq. 2). However, the humidity effect was not as significant as in Nafion because the humidity dependence of these kinds of PBI-type membranes was much lower than that of Nafion [20].



Proton transport phenomena in doped-PBI membrane occur mainly via two ways: One is based on the rapid proton exchange (hopping) between the phosphonate and imidazole moieties via hydrogen bonds and donor (amine)–acceptor (imine) principle, and the other is based on the self-diffusion of phosphonate moieties. Moreover, thiophene being basic in nature interacts with proton or undergoes proton doping. As a result, availability of proton in the system is more resulting improved proton conductivity as shown in Scheme 1. The proton conductivity of PBI-type membrane is enhanced with

increasing temperature due to the increased activation energy of proton transport [21, 22].

The activation energies (E_a) for the proton conduction behavior in the membranes are calculated by the Arrhenius equation (Eq. 3);

$$\ln \sigma = \ln \sigma_0 - \frac{E_a}{RT} \quad (3)$$

where R , T and σ_0 are the gas constant, the absolute temperature and the frequency factor (independent of T), respectively. The activation energy values are calculated from the slope of the straight line obtained from the plot of $\ln \sigma$ against T^{-1} (Fig. 3). As it is observed for the doped-PBI membranes, the proton conduction in DPBITH membranes is likely to occur due to proton hopping between PA, phosphate ions, absorbed water and positively charged imidazole rings and thiophene rings (Grotthuss mechanism) [9, 23, 24]. Water is an active element in proton hopping inside the electrolyte. This causes an increase in the proton conductivity with a proportionate reduction in the activation energy with increased RH [21, 25]. The

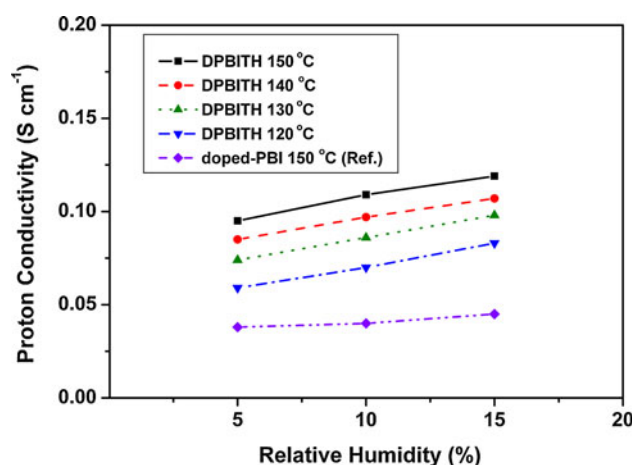
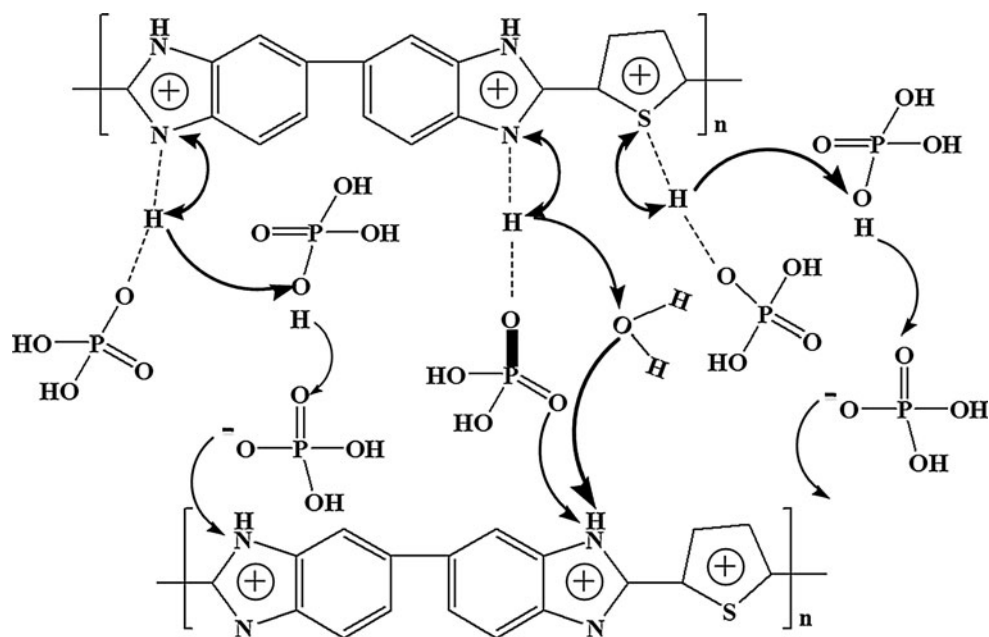


Fig. 3 Proton conductivities of DPBITH and doped-PBI (reference) membranes at different temperatures and humidities

Scheme 1 Scheme of the proton transport mechanism of DPBITH



activation energy of the DPBITH membrane at 5 % RH is 21.7 kJ mol^{-1} , which is lower than or close to the previously reported values [20, 26]. The activation energy of the DPBITH membrane is drastically reduced at 15 % RH. This is due to the decrease in the proton hopping process upon equilibrating the membrane in more humid environments caused by the participation of water in the proton conduction process [22]. These results suggest that the DPBITH membrane reported in this work holds great promise for use in high-temperature PEMFC applications.

4 Conclusions

A PBITH membrane was synthesized through the condensation polymerization of DAB and TDA. The benzene ring in the PBI-type membrane was replaced by a thiophene ring in order to increase the basicity of the polymer backbone and to enhance the interaction of PA with the polymer. The DPBITH membrane had a reasonable proton conductivity value (0.120 S cm^{-1}) at 150°C and 15 % RH. The proton conductivity of the DPBITH membrane was much higher than that of the doped-PBI membrane. An increase in the RH from 5 to 15 % resulted in a decrease in the activation energy of the membrane from 21.7 to 16.2 kJ mol^{-1} . Despite the low mechanical properties of the DPHITH, this class of thiophene-based PBI membrane holds great promise for its use in high-temperature applications.

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